Hydrogen on Cobalt: The Effects of Carbon Monoxide and Sulphur Additives on the D₂/Co(0001) System

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Abstract

Hydrogen reaction on catalytic surfaces is an important field of research in fuel cell science. The adsorption of hydrogen (deuterium) on Co(0001) and the influence of carbon monoxide and sulphur on the adsorption were studied by XPS, TDS, WF measurements and LEED. The WF increased due to D_2 adsorption, revealing the electronegative character of deuterium. It was found that the deuterium saturation coverage is ~ 0.17 ML at 320 K and ~ 0.27 ML at 180 K. The activation energy for desorption was estimated to be 33 kJ/mol. The coadsorption measurements with CO indicated a decrease in the deuterium yield by 50%. A downward shift of 50 K in the deuterium desorption temperature was observed as a consequence of coadsorbed CO, but changes in the CO desorption were minimal. At small CO exposures the (2×2) LEED structure of deuterium was seen, while at exposures of above 5 L the $(2\sqrt{3} \times 2\sqrt{3})R30\ldots$ structure was detected by LEED as with pure CO adsorption. Coadsorption with sulphur led also to a decrease in the D_2 yield leading to a complete inhibition of hydrogen adsorption at sulphur saturation. The sulphur (2×2) LEED structure did not underwent changes due to deuterium adsorption. As assumed, sulphur worked as a strong poison to the adsorption on Co(0001).

1. Introduction

The understanding of catalytic processes has improved remarkably during the last 30 years. The standard case in surface studies related to catalysis has been the carbon monoxide molecule on transition metal surfaces. On the other hand, hydrogen, which is equally important in many catalytic processes, has not been studied as extensively in surface science. The main reasons for that are the high mobility of hydrogen and the relatively difficult and restricted measurement possibilities with electron spectroscopies.

Adsorption of hydrogen on cobalt has mainly been studied with supported catalysts and thin films [1–11]. Bartholomew and co-workers have published several papers on the adsorption of hydrogen and CO on supported cobalt catalysts [5–7]. Vannice reported on the catalytic synthesis of hydrocarbons from H_2/CO mixtures using supported group VIII metal catalysts at 1 atm total pressure [8,9]. Dus and Lisowski studied the hydrogen adsorption on evaporated cobalt films at 78 K and at 195 K [10]. Ernst et al. showed that pure hydrogen adsorption on Co(10$\bar{1}$0) between 90 and 200 K takes place dissociatively and three different structures are formed depending on the coverage. In TD spectra two desorption stages were distinguished with peak maxima around 260 K and 310 K [11].

Understanding how hydrogen reacts with surface atoms and adsorbed atoms on the surface is important in several scientific fields: heterogeneous catalysis, hydrogen storage, material science and fuel cell research. In the later one there is an increased demand for new materials. One of the main topics in fuel-cell-related studies is the synthesis of hydrogen from gasoline or methanol inside the automobile. As it is shown in our earlier study, hydrocarbon fuels, like methanol, dissociate on the Co(0001) surface entirely to H_2 and CO [12]. This property connected with the low cost of the material, makes cobalt—additionally to its importance as a Fisher–Tropsch catalyst—one of the most promising materials for fuel cell research.

In our research we used thermal desorption spectroscopy, X-ray photoelectron spectroscopy, low energy electron diffraction and work function measurements to investigate the adsorption behaviour of D_2 on a cobalt single crystal. In this study, the reactions of pure hydrogen and hydrogen coadsorbed with CO on Co(0001) are one part of the research. The other part deals with the changes in the hydrogen adsorption by adding pre-adsorbed S. This is of special interest as hydrocarbon fuels always contain small amounts of sulphur compounds, which tend to poison the catalytic behaviour of the system. The influence of sulphur on the hydrogen adsorption on transition metals has been studied before, e.g., on Pt: here sulphur was found to decrease the amount of adsorbed hydrogen on platinum due to site blocking as well as by electrostatic repulsion [13].

2. Experimental

The experiments were carried out in an UHV stainless-steel chamber with base pressure of $2 \cdot 10^{-10}$ Torr. The chamber contained facilities for X-ray photoelectron spectroscopy (XPS), thermal desorption spectroscopy (TDS) and low energy electron diffraction (LEED) measurements.

Deuterium (AGA, 99.8%), carbon monoxide (AGA, 99.997%) and hydrogen sulphide (AGA, 99.8%) were used as received. The sulphur overlayer was prepared by depositing H_2S at the desired temperature followed by annealing to 650 K. During annealing hydrogen was removed from the surface and a pure sulphur layer was obtained.

As a sample a disc-shaped Co(0001) single crystal was used, having a diameter of 11 mm. The Co(0001) sample was fixed to the sample holder by 0.25 mm tantalum wires, which were also used for resistive heating and conducting

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heat to the heat sink cooled with liquid nitrogen. This set-up allowed cooling the sample down to 160 K. The maximum temperature was restricted to around 690 K, by the hcp-fcc phase transition temperature of cobalt. The temperature of the sample was continuously monitored by using a chromel-alumel thermocouple spot welded directly on the sample surface. For a detailed description of the apparatus and initial cleaning procedure the reader is referred back to our previous published works [14–16].

The procedure to obtain a clean surface before each experiment was the following: First the cobalt surface was sputtered with 1 keV Ar^+-ions for about 1 h at room temperature. Then sputtering was continued while heating the sample up to about 600 K. After 20 min the sputtering process was stopped and subsequently the sample was annealed for additional 20 min at $\sim$ 640 K. The cleanliness was confirmed by XPS and LEED measurements. After cleaning, the sample was cooled down to the desired temperature of exposure. The gases were admitted in the UHV chamber through leak valves. After exposure optional XPS, TDS or LEED measurements were performed. In XPS measurements the sample was biased with a small negative voltage to ensure that the measured data originate from the sample only. TDS measurements were performed with linear heating rates ranging from 2.6–3.5 K/s in the cases of pure D_2 and D_2/CO to 7 K/s in the case of S/D_2 adsorption.

3. Results and discussion

3.1. Adsorption of D_2 on Co(0001)

In this work we studied the deuterium adsorption on Co(0001) at 320 and 180 K. Deuterium was used as a substitute for hydrogen to avoid any artifacts due to the background hydrogen in the chamber.
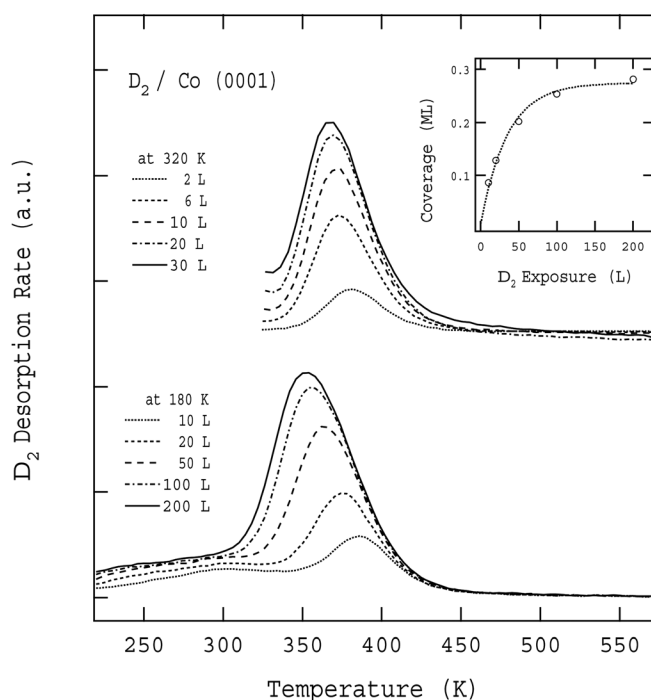
Work function (WF) measurements confirmed the electronegative character of deuterium on cobalt, showing an increase of 200 mV due to D_2 adsorption. This value is in good agreement with WF changes between 170 and 220 mV found for several H_2/Pd systems [17].

Figure 1 shows the desorption of deuterium molecules (4 amu) from D_2 exposed clean Co(0001) at 320 and 180 K for increasing exposures. Clearly only one desorption peak developed with adsorption at both exposure temperatures. The second order desorption process is verified by the symmetric peak shape and by the peak shift to lower temperature with increasing coverage. D_2 desorbs from the surface between 300 and 450 K with the peak temperature decreasing from 380 to 350 K with increasing coverage. Additionally the 180 K adsorption peak is distinguished by a shoulder on the low temperature side of the spectrum.

Our results in Fig. 1 indicate that the adsorption of hydrogen on Co(0001) is not an activated process: With increasing temperature of exposure a decreasing amount of deuterium was adsorbed, indicating that the activation energy for desorption is determining the surface coverage. Our result of non-activated adsorption is in line with a recent calculation of the same system [18]. The TDS data showed that the desorption started at lower temperatures for temperature of exposure of 180 K than for 320 K. This together with the increasing desorption yield with decreasing adsorption temperature clearly indicates that at room temperature not all the adsorption sites are in use. The relationship between desorption yield (coverage) and temperature of exposure is shown in Fig. 2. Above room temperature the coverage is very small. With decreasing temperature the coverage of D_2 is increasing and saturates at a value of $\sim$0.27 ML at temperatures below 250 K.

The desorption kinetics were estimated with the help of the TDS data according to Redhead [19]. The low desorption temperatures show that the binding energy between deuterium and cobalt is small. The activation energy for desorption of D_2 was calculated to be only
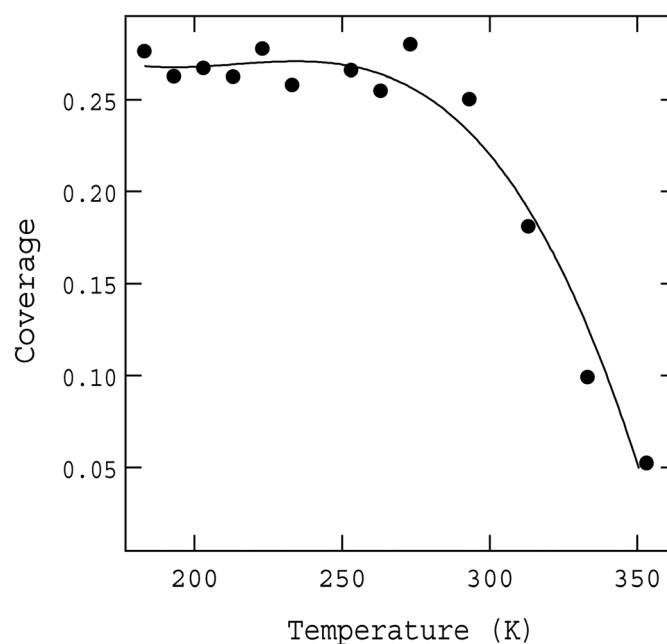

Fig. 1. TDS peaks of various amounts of deuterium after adsorption at 180 and 320 K. The heating rates at 320 and 180 K were 2.6 K s⁻¹ and 3.5 K s⁻¹, respectively. The dependence of the deuterium coverage at 180 K on the D_2 exposure is shown in the inset.

Fig. 2. TDS yield of D_2 as a function of adsorption temperature after exposure to 200 L of D_2; corresponding to saturation exposure. The line is shown to guide the eye.

33–0.6 kJ/mol. This value fits well to the results found for hydrogen desorption from polycrystalline platinum (18–39 kJ/mol) and Ru(0001) with 46 kJ/mol [13,20].

The coverage of deuterium molecules as a function of D_2 exposure at 180 K is plotted in the inset of Fig. 1. The coverage was scaled by linking the TDS peak area of dideuterium to another hydrogen containing molecule, with a known coverage. For this reference, measurements of acetylene adsorption on the Co(0001) were performed. Previously, this system had been studied to some extend by our group [21]. The adsorption of acetylene on clean Co(0001) at room temperature took place molecularly, but during the desorption the molecule decomposed. The saturation coverage was measured in this work by following with XPS the C1s signal as a function of acetylene exposure at 320 K. The C1s signals at saturation of acetylene and at saturation of CO were compared and the results gave a peak area ratio of 2.0–0.1 indicating equal saturation coverage of 1/3 for carbon monoxide and acetylene. The complete dissociation of C_2H_2 during heating resulting in a hydrogen desorption peak in TDS, was then utilised for comparison to the dideuterium TD peak in this study. The integrated area of the dideuterium TDS peak was about 50% of the acetylene peak measured under the same circumstances. The resulting deuterium saturation coverage was estimated to be 0.17 ML at 320 K and about 0.27 ML at 180 K. At the lower temperature we also observed a (2×2) adsorption structure on the surface. The LEED pattern was faint and not reproducible at every attempt, probably due to the damage caused by the electron beam. It thus seems that the formation of the structure is very sensitive to all possible disturbing effects. Especially the high mobility of deuterium atoms at these temperatures increases the sensitivity of this structure to damage. However, the ordered (2×2) structure at 180 K corresponds to the coverage of 0.25 ML, which supports the value for saturation coverage obtained in comparison with acetylene.

3.2. *The effect of CO on D2 adsorbed on the surface*

The effect of CO on D_2 was studied at 180 K by precovering the surface with 200 L of deuterium and then exposing the surface to increasing amounts of CO. XPS as well as WF measurements gave the same results as in the case of CO adsorption on clean cobalt. The amount of adsorbed CO—on the clean and on the deuterium covered Co(0001) surface—increases in both cases up to the saturation level.

Figure 3 (a) and (b) illustrate the interaction of coadsorbed deuterium and CO by means of a series of TDS spectra. The spectrum of pure deuterium after saturation is shown as a reference.

Figure 3(a) shows the effect of CO on the dideuterium TD peak, which clearly shifts towards lower temperatures with increasing CO exposure. A reduction in the position of the TDS-peak maximum from 360 K of the pure deuterium spectrum to 300 K after 2 L CO exposure is observed. Furthermore, the shoulder at 260 K diminishes with CO exposure and vanishes at 5 L CO. The desorption yield of deuterium decreases continuously and saturates to the value of $\sim$50% of the initial TDS yield at 5 L CO exposure, showing that during the exposure of carbon
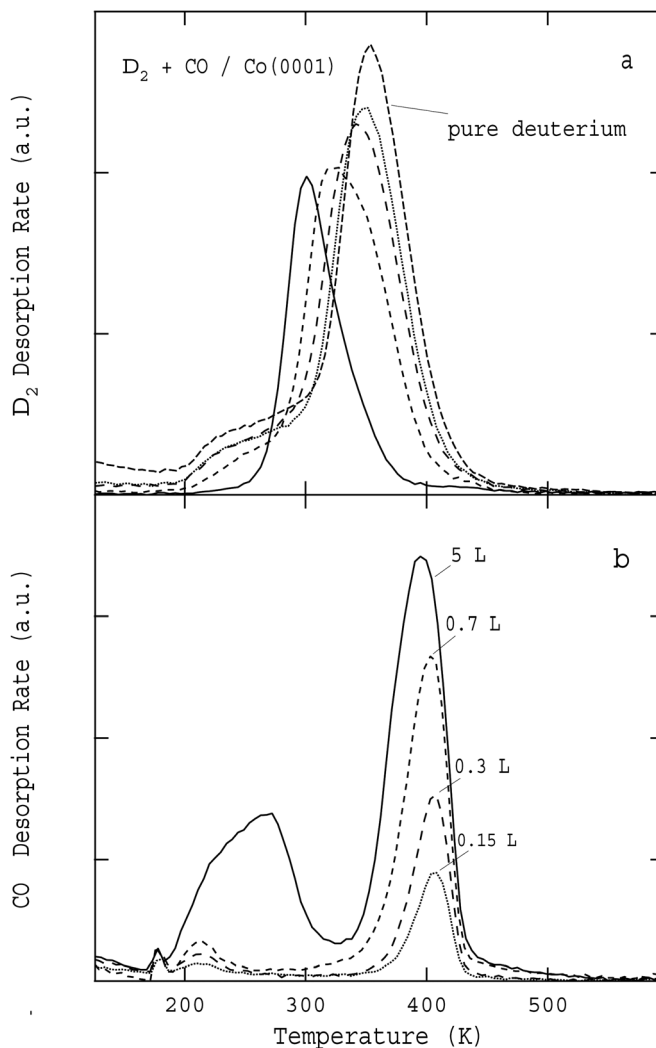

Fig. 3. TDS spectra of D_2 (a) and CO (b) after various CO exposures on Co(0001) surface precovered with 200 L of D_2. The CO exposures are given in the figure and they are the same for both sets of data. For comparison the D_2 only and the CO only TD spectra are also shown. The heating rate was 3.5 K/s.

monoxide only a fraction of the pre-adsorbed D_2 desorbed from the surface. This should be expected since cobalt can be used as catalyst for CO hydrogenation reactions. Further CO deposition does not cause any spectral changes. We explain the decrease in the deuterium yield by repulsive interaction of CO and deuterium atoms.

In Fig. 3(b) it is seen that the desorption maximum of the CO peak is shifted from 410 to 390 K with increasing CO exposure up to 5 L. A similar behaviour was also seen with CO adsorption on clean Co(0001) [22]. The shift can be explained by the repulsive dipole–dipole interaction between the CO molecules, which is playing a more important role with increasing CO coverage. With higher exposures a second desorption feature becomes visible around 270 K. This second feature has also been seen with CO adsorption on Co(0001) where the desorption from the $(2\sqrt{3} \times 2\sqrt{3})R30 - 7CO$ structure gave rise to a desorption maximum at 250 K. However, the peak shape and its position are somewhat different with the D_2 precovered surface. The LEED investigation of the coadsorption structure indicated the formation of the $(2\sqrt{3} \times 2\sqrt{3})R30$ structure, best visible after 5 L of CO. By comparing the area of the CO peaks after saturation exposure of CO, we concluded that the amount of adsorbed CO does not

depend on the D_2 precoverage. The D_2 precoverage also results in the absence of the $(\sqrt{7/3} \times \sqrt{7/3})R10.9$ structure, which is known from the pure CO adsorption [22]. Since it is suggested that this structure is due to mutual stabilisation between the CO molecules, it supports our assumption that hydrogen and CO interact repulsively and cause mutual destabilisation.

Coadsorption in general can result in attractive or repulsive adsorbate interactions, depending on the chemical nature of the adsorbed species. On first sight coadsorption of CO and deuterium should result in an attractive interaction and mutual stabilisation of the adsorbed species, based on the location of hydrogen in the alkali metal (AM) group in the periodic table and the known acceptor behaviour of CO on transition metals. This mutual stabilisation has been observed for alkali metals [16,23,24]. In the case of COAM coadsorption, the adsorbed species are effectively stabilising each other and this is featured by the simultaneous desorption of both species at higher temperature than they would desorb from the clean surface.

H however is known to be able to act both as electron donor and acceptor, also indicated by its higher electronegativity compared to alkali metals. For pure D_2 adsorption, the WF increase was attributed to the electron acceptor behaviour of deuterium on cobalt. In the case of $D_2 + CO$ coadsorption both coadsorbed species act as electron acceptors, which is one reason for the shift of the desorption-peak maxima to lower temperatures. Beside the repulsive interaction between CO and deuterium, one additional reason for this behaviour is the high mobility of deuterium facilitating their displacement by less mobile molecules, like CO. Repulsive intermolecular forces and the fact that with increasing coverage also less favourable energetic sites are getting occupied, cause the shift to lower temperatures.

3.3. The effect of sulphur on D_2 adsorption

The clean cobalt surface was exposed to various amounts of H_2S at RT. The hydrogen sulphide was directed to the sample surface using a doser pipe close to the surface, to avoid unnecessary backfilling of the chamber. To decompose the H_2S molecules to a pure sulphur overlayer, the sample was subsequently annealed to 650 K. The saturation coverage of sulphur at RT was determined to be 1/3 ML. The WF undergoes a surprisingly little change due to the adsorption of sulphur. Only an increase of 0.2 eV was found for saturation coverage. This value is in accordance with the WF change of 0.2–0.4 eV found for Ni(100) [25,26]. The WF did not change with subsequent deuterium exposure.

The sulphur-covered surface was exposed to 200 L of deuterium at RT. During TD dideuterium was the only gaseous product evolved. Specifically, no desorption of sulphur containing molecules was found. Additionally, XPS measurements confirmed that the sulphur atoms stay on the surface. The changes in the D_2 desorption peak, as a result of increased sulphur precoverage, are displayed in Fig. 4. For comparison, we report the dideuterium spectrum recorded for desorption from clean Co(0001) in the same figure. In this case a single TD state develops about 375 K, having a slightly different temperature
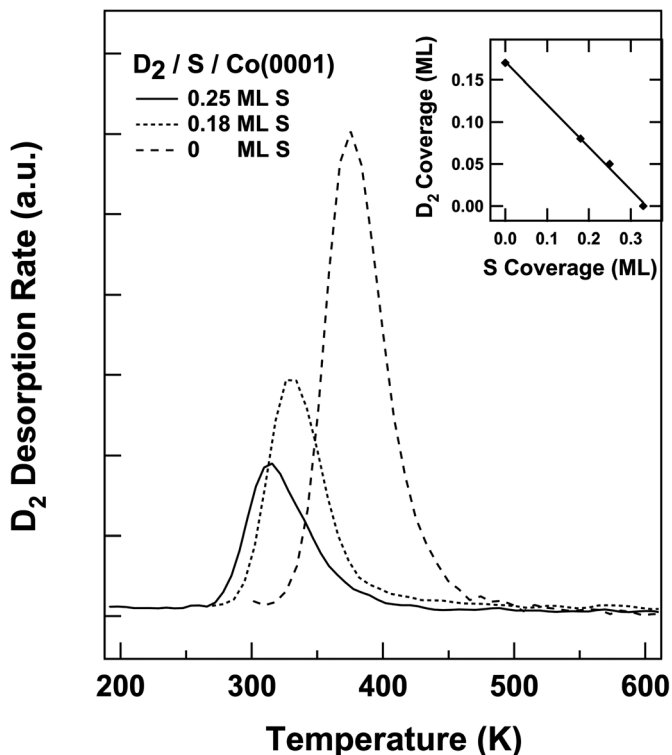

Fig. 4. The TDS signal for 200 L of D_2 for increasing pre-exposure of sulphur. The heating rate is 7 K/s. The inset shows the linear dependency of the D_2 coverage (desorption yield) on the sulphur precoverage. The line is drawn to show the trend.

maximum than the peak in 3.1 due to the different heating rate.

Already for small sulphur precoverage the TD peak of dideuterium gradually shifts to lower temperatures reaching 290 K with 0.25 ML of sulphur. Simultaneously the peak size is reduced by a factor of three of the original dideuterium peak. At sulphur saturation no deuterium adsorption takes place.

Hydrogen sulphide showed a bright (2×2) diffraction pattern after exposing the clean cobalt sample to 0.25 ML of H_2S. No reconstruction occurred upon annealing to 650 K as a result of simultaneous dihydrogen desorption. There was no evidence for reconstruction or appearance of additional LEED spots due to subsequent D_2 adsorption. Since the TDS measurements revealed that with 0.25 ML of sulphur D_2 adsorption still takes place on the surface, we conclude there is no long-range ordering of hydrogen due to sulphur.

We found that small amounts of preadsorbed sulphur led to a drastic decrease in the dideuterium TD yield as well as a shift of the dideuterium desorption peak to lower desorption temperatures: The reduction in the desorption temperature has its origin in the destabilisation of adsorbed hydrogen by sulphur. Due to sulphur, hydrogen has to adsorb on energetically unfavourable adsorption sites, leading to the obtained shift in the TDS peak. The decrease in the amount of adsorbed deuterium is also reflected in the WF, as the amount of adsorbed deuterium is so small that no changes in the WF are registered. sulphur saturation exposure inhibits completely the adsorption of H. A plausible explanation for the reduction in the dideuterium area is the blocking of deuterium adsorption sites by sulphur. The site blocking due to sulphur can be seen in the inset of Fig. 4. The straight line is what should be expected

for direct local site blocking. As sulphur does not leave the surface during heating, it works as a strong poison to hydrogen containing processes.

4. Conclusions

We have studied the behaviour of hydrogen (deuterium) on cobalt surfaces. On cobalt deuterium rapidly adsorbs and dissociates with a small binding energy of 33 kJ/mol. hydrogen (deuterium) acts on cobalt as an electron acceptor, leading to an increase in the WF by 200 mV. The saturation coverage was estimated to be 0.17 ML at 320 K and 0.27 ML at 180 K. Our results show furthermore that hydrogen adsorption on cobalt is not an activated process.

In the coadsorption of CO and D_2 CO easily replaces deuterium. Due to the displacement and repulsive interactions between CO and deuterium atoms, the amount of adsorbed deuterium steadily decreases with increasing CO coverage. 50% of the original amount of deuterium on the catalyst surface is found for CO saturation.

The decrease in the D_2 yield as a function of sulphur coverage illustrates blocking of adsorption sites. sulphur, with the same saturation coverage as CO, leads to a complete inhibition of hydrogen adsorption. As sulphur is not as easily removed from the catalyst surface as CO, sulphur works as an actual poison for the hydrogen adsorption on cobalt.

Acknowledgments

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